

# PAMOP project: computations in support of experiments and astrophysical applications

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**Abstract** Our computation effort is primarily concentrated on support of current and future measurements being carried out at various synchrotron radiation facilities around the globe, and photodissociation computations for astrophysical applications. In our work we solve the Schrödinger or Dirac equation for the appropriate collision problem using the R-matrix or R-matrix with pseudo-states approach from first principles. The time dependent close-coupling (TDCC) method is also used in our work. A brief summary of the methodology and ongoing developments implemented in the R-matrix suite of Breit-Pauli and Dirac-Atomic R-matrix codes (DARC) is presented.

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## 1 Introduction

Our research efforts continue to focus on the development of computational methods to solve the Schrödinger and Dirac equations for atomic and molecular collision processes. Access to leadership-class computers such as the Cray XC40 at HLRS allows us to benchmark our theoretical solutions against dedicated collision experiments at synchrotron facilities such as the Advanced Light Source (ALS), Astrid II, BESSY II, SOLEIL and PETRA III and to provide atomic and molecular data for ongoing research in laboratory and astrophysical plasma science. In order to have direct comparisons with experiment, semi-relativistic, or fully relativistic computations, involving a large number of target-coupled states are required to achieve spectroscopic accuracy. These computations could not be even attempted without access to high performance computing (HPC) resources such as those available at leadership computational centers in Europe (HLRS) and the USA (NERSC, NICS and ORNL). We use the R-matrix and R-matrix with pseudo-states (RMPS) methods to solve the Schrödinger and Dirac equations for atomic and molecular collision processes.

Satellites such as *Chandra* and *XMM-Newton* are currently providing a wealth of x-ray spectra on many astronomical objects, but a serious lack of adequate atomic data, particularly in the *K*-shell energy range, impedes the interpretation of these spectra. With the break-up and demise of the recently launched *Astro-H* satellite in the spring of 2016, it has left a void in x-ray observational data for a variety of atomic species of prominent astrophysical interest of paramount importance (Kallman T, Private communication, 2015). In the intervening period before the next x-ray satellite mission, we shall continue to benchmark laboratory photoionization cross section measurements against sophisticated theoretical methods.

The motivation for our work is multi-fold; (a) Astrophysical Applications [1, 2, 3, 4], (b) Fusion and plasma modelling, (c) Fundamental interest and (d) Support of experimental measurements and Satellite observations. For heavy atomic systems [5, 6], little atomic data exists and our work provides results for new frontiers on the application of the R-matrix; Breit-Pauli and DARC parallel suite of codes. Our highly efficient R-matrix codes are widely applicable to the support of present experiments being performed at synchrotron radiation facilities. Examples of our results are presented below in order to illustrate the predictive nature of the methods employed compared to experiment.

The main question asked of any method is, how do we deal with the many body problem? In our case we use first principle methods (ab initio) to solve our dynamical equations of motion. Ab initio methods provide highly accurate, reliable atomic and molecular data (using state-of-the-art techniques) for solving the Schrödinger and Dirac equation. The R-matrix non-perturbative method is used to model accurately a wide variety of atomic, molecular and optical processes such as; electron impact ionization (EII), electron impact excitation (EIE), single and double photoionization and inner-shell x-ray processes. The R-matrix method provides cross sections and rates used as input for astrophysical modeling codes such as; CLOUDY, CHIANTI, AtomDB, XSTAR necessary for interpreting experiment/satellite obser-

variations of astrophysical objects as well as fusion and plasma modeling for JET and ITER.

## 2 R-matrix code performance: Photoionization

The use of massively parallel architectures allows one to do calculations which previously could not have been addressed. This approach enables large scale relativistic calculations for trans-iron elements of Kr-ions, Xe-ions, Se-ions [5, 6] and W-ions [10, 11]. It allows one to provide atomic data in the absence of experiment, and for that purpose takes advantage of the linear algebra libraries available on most architectures.

**Table 1** Photoionization cross section calculations: timings for the  $J = 1$  scattering symmetry of  $W^{2+}$  ions. The scattering model used included 392-states, 1,728 coupled channels, and 800,000 energy points. The R-matrix outer region module PSTGBF0DAMP performance on Hazel Hen, the Cray-XC40 at HLRS, is presented for a different number of cores.

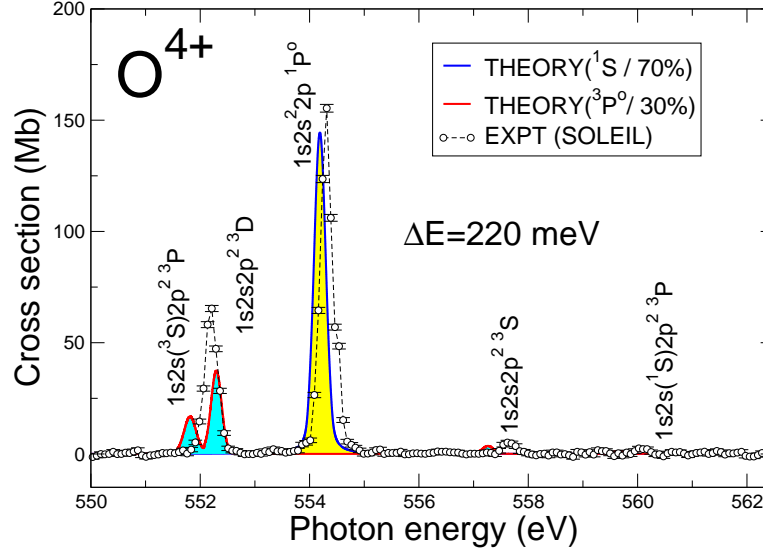
R-matrix (Module)	Number of runs	Speed-up (factor)	Cray XC40 (Number of cores)	Total core time (minutes)
PSTGBF0DAMP	1	1.00	1,000	451.525
PSTGBF0DAMP	1	2.01	2,000	224.588
PSTGBF0DAMP	1	3.93	4,000	114.866
PSTGBF0DAMP	1	5.82	8,000	77.523
PSTGBF0DAMP	1	9.77	10,000	46.193

Further developments of the dipole codes benefit from similar developments made to the existing excitation R-matrix codes [6, 7, 8, 9]. In Table 1 we show typical timings required in the determination of the photoionization cross section results for  $W^{2+}$  ions, for the  $J=1$  even scattering symmetry. Timings and speed up factors are given for the outer region module PSTGBF0DAMP used to determine photoionization cross sections. One clearly sees that using between 1,000 to 10,000 cores, a speed up of nearly a factor of 10 is obtained with almost perfect scaling of this outer region module.

## 3 X-ray and Inner-Shell Processes

### 3.1 K-shell Photoionization of Atomic Oxygen Ions: $O^{4+}$ and $O^{5+}$

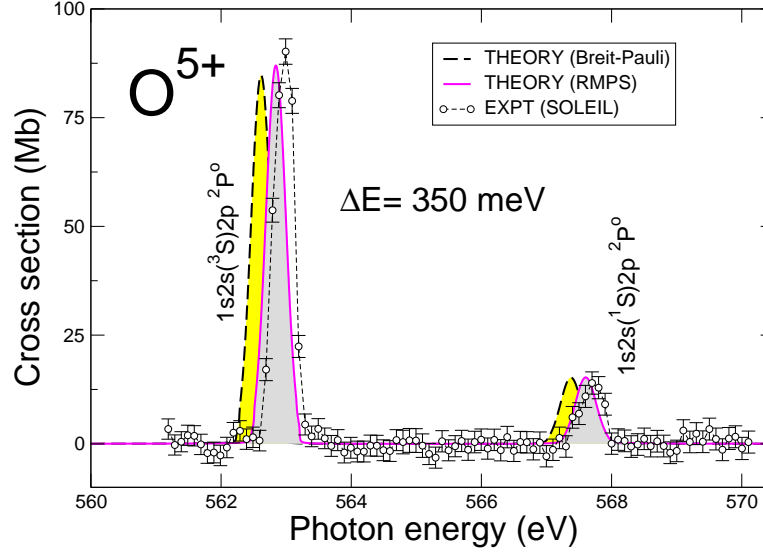
The launch of the satellite Astro-H (re-named Hitomi) on February 17, 2016, was expected to provide x-ray spectra of unprecedented quality and would have required



**Fig. 1** SOLEIL experimental  $K$ -shell photoionization cross section of  $O^{4+}$  ions in the 550 - 560 eV photon energy range. Measurements were taken with a 220 meV band-pass at FWHM [22]. Solid points (experiment): the error bars give the statistical uncertainty. Solid line (R-matrix with pseudostates 526-levels) assuming an admixture of 70% ( $1s^2 2s^2 \ ^1S$ ) and 30 % ( $1s^2 2s 2p \ ^3P^o$ ). The strong  $1s \rightarrow 2p$  resonances are clearly visible in the spectra.

a wealth of atomic and molecular data on a range of collision processes to assist with the analysis of spectra from a variety of astrophysical objects. The subsequent break-up 40 days later on March 28, 2016 of *Hitomi* leaves a void in observational x-ray spectroscopy. Measurements of cross sections for photoionization of atoms and ions are essential data for testing theoretical methods in fundamental atomic physics and for modeling of many physical systems, for example, terrestrial plasmas, the upper atmosphere, and a broad range of astrophysical objects (quasar stellar objects, the atmosphere of hot stars, proto-planetary nebulae, H II regions, novae, and supernovae) [12, 13].

Limited wavelength observations for x-ray transitions were recently made on atomic oxygen, neon, magnesium and their ions with the High Energy Transmission Grating (HETG) on board the *CHANDRA* satellite [14]. Strong absorption  $K$ -shell lines of atomic oxygen, in its various forms of ionization, have been observed by the XMM-Newton satellite in the interstellar medium, through x-ray spectroscopy of low-mass x-ray binaries [15]. The Chandra and XMM-Newton satellite observations may be used to identify absorption features in astrophysical sources, such



**Fig. 2** SOLEIL experimental  $K$ -shell photoionization cross section of  $O^{5+}$  ions in the 560 - 570 eV photon energy range. Measurements were taken with a 350 meV band-pass at FWHM [22]. Solid points (experiment): the error bars give the statistical uncertainty. Solid (magenta) line R-matrix with pseudostates, 120-levels for the  $1s^2 2s^2 S$  ground state. Dashed (black) line Breit-Pauli approximation. The strong  $1s \rightarrow 2p$  resonances are clearly visible in the spectra.

as active galactic nuclei (AGN), x-ray binaries, and for assistance in benchmarking theoretical and experimental work [16, 17, 18, 19, 20, 21].

Absolute cross sections for the  $K$ -shell photoionization of Be-like ( $O^{4+}$ ) and Li-like ( $O^{5+}$ ) atomic oxygen ions were measured (in their respective  $K$ -shell regions) by employing the ion-photon merged-beam technique at the SOLEIL synchrotron-radiation facility in Saint-Aubin, France. High-resolution spectroscopy with  $E/\Delta E \approx 4000$  ( $\approx 140$  meV, FWHM) was achieved with photon energy from 550 eV up to 675 eV. Rich resonance structure observed in the experimental spectra is analyzed using the R-matrix with pseudostates (RMPS) method.

Detailed spectra for Be-like [ $O^{4+}$ ] and Li-like [ $O^{5+}$ ] atomic oxygen ions in the vicinity of the  $K$ -edge were measured. This work is the culmination of photoionization cross section measurements on the atomic oxygen isonuclear sequence. Previous studies on this sequence, focused on obtaining photoionization cross sections for the  $O^+$  and  $O^{2+}$  ions [17] and the  $O^{3+}$  ion [16], where differences of 0.5 eV in the positions of the  $K_\alpha$  resonance lines with prior satellite observations were found. This will have major implications for astrophysical modelling.

Fig. 1 shows the spectra for Be-like atomic oxygen in the region of the strong  $1s \rightarrow 2p$  resonance. To compare directly with the SOLEIL measurements, the theoretical R-matrix cross sections have been convoluted with a Gaussian profile width of 220 meV at FWHM. For  $O^{4+}$  as the  $1s^2 2s 2p^3 P^0$  metastable state is present in the photon beam, an admixture of 70% of the ground state and 30% of the metastable state, of the respective cross sections, appears to simulate experiment suitably well. The theoretical cross section results presented in Fig. 1 indicate excellent agreement with the SOLEIL experimental measurements. Similarly in Fig. 2, the SOLEIL spectra for Li-like atomic oxygen in the region of the strong  $1s \rightarrow 2p$  resonance are illustrated. To compare with the SOLEIL measurements, the theoretical cross sections have been convoluted with a Gaussian profile width of 350 meV at FWHM. We note that for both ions, the theoretical results from the R-matrix with pseudostates method (RMPS) show suitable agreement with the SOLEIL measurements [22].

### 3.2 *L-shell Photoionization: $Ar^+$*

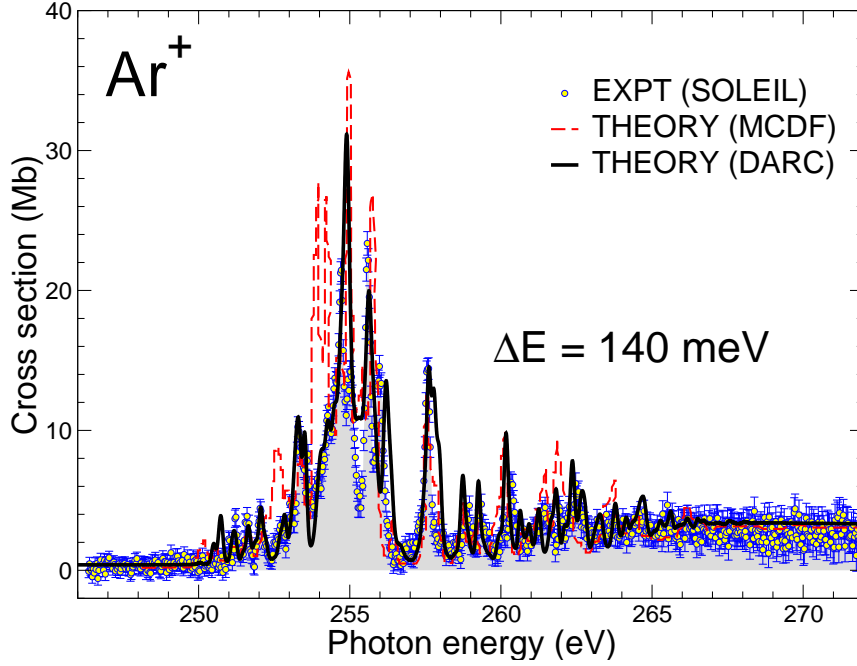
Photoionization cross-sections were obtained using the relativistic Dirac Atomic R-matrix Codes (DARC) for valence and *L*-shell energy ranges between 27 and 270 eV. A total of 557 levels arising from the dominant configurations  $3s^2 3p^4$ ,  $3s 3p^5$ ,  $3p^6$ ,  $3s^2 3p^3 [3d, 4s, 4p]$ ,  $3p^5 3d$ ,  $3s^2 3p^2 3d^2$ ,  $3s 3p^4 3d$ ,  $3s 3p^3 3d^2$ ,  $2s^2 2p^5$  and  $3s^2 3p^5$  have been included in the target wavefunction representation of the residual  $Ar^{2+}$  ion, including up to  $4p$  in the orbital basis. The target wavefunctions were obtained using the GRASP code [23, 24], and the collision calculations were performed using a parallel version of the DARC codes [7, 8, 9, 26]. Direct comparisons of the photoionization cross sections in the valence region showed excellent agreement with previous R-matrix results and ALS measurements [27].

Photoionization cross section calculations were performed in the *L*-shell energy region between 250 and 280 eV in order to compare directly with the measurements made by Bizau and co-workers at the SOLEIL radiation facility in France [28]. To compare directly with the SOLEIL measurements, theory was convoluted with a 140 meV Gaussian profile width at FWHM to match the experiment.

Fig. 3 illustrates the photoionization cross-section, as a function of the incident photon energy in eV across the *L*-shell threshold region from 250 to 270 eV. Comparisons are made between the experimental results from SOLEIL, and theoretical work, MCDf and DARC. In order to match the SOLEIL experimental spectrum an energy shift of 7.5 eV to the DARC calculations was necessary [29].

### 3.3 *Photoionization of Tungsten (W) Ions: $W^{2+}$ and $W^{3+}$*

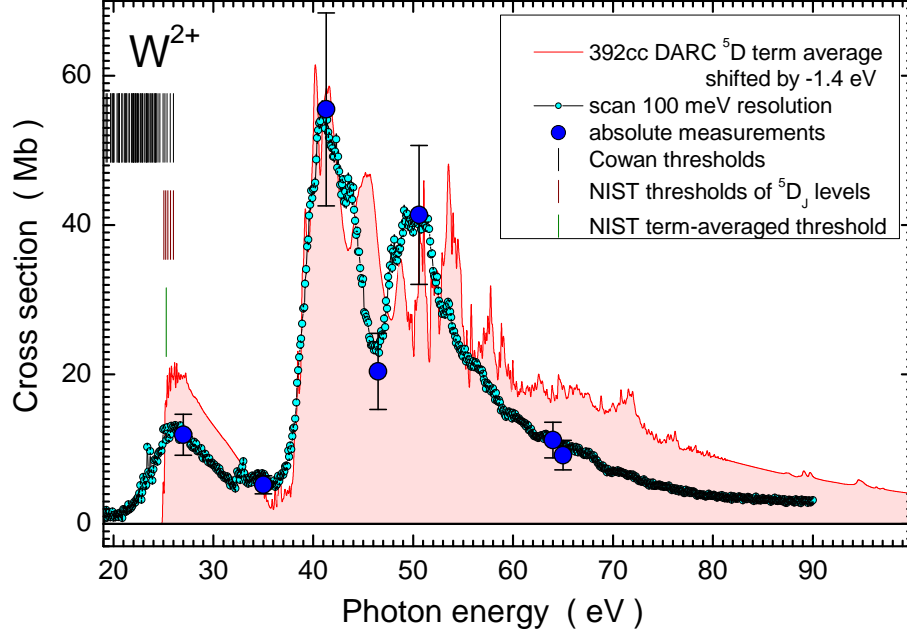
Although not directly relevant to fusion, photoionization of tungsten atoms and ions is interesting because it can provide details about spectroscopic aspects and,



**Fig. 3** Photoionization cross sections (Mb) as a function of the photon energy (eV) in the  $\text{Ar}^+$  L-shell region between 250 and 270 eV. The (blue) circles are the experimental measurements from SOLEIL taken at a band pass of 140 meV at FWHM. The dashed (red) line are the MCDF theoretical results and the solid (black) line are the DARC (model DARC3) results. The theoretical results were statistically weighted for the initial ground state and convoluted with a Gaussian profile width of 140 meV at FWHM [29].

as time-reversed photorecombination, provides access to the understanding of one of the most important atomic collision processes in a fusion plasma, electron-ion recombination. R-matrix theory is a tool to obtain information about electron-ion and photon-ion interactions in general. Electron-impact ionization and recombination of tungsten ions have been studied experimentally [30, 31, 32, 33, 34, 35, 36, 37] while there are no detailed measurements on electron-impact excitation of tungsten atoms in any charge state. Thus, the present study on photoionization of these complex systems and comparison of the experimental data with R-matrix calculations provides benchmarks and guidance for future theoretical work on electron-impact excitation.

For comparison with the measurements made at the ALS, state-of-the-art theoretical methods using highly correlated wavefunctions were applied that include relativistic effects. An efficient parallel version [10, 11] of the DARC [25, 24, 26] suite of codes continues to be developed and applied to address electron and photon interactions with atomic systems, providing for hundreds of levels and thousands

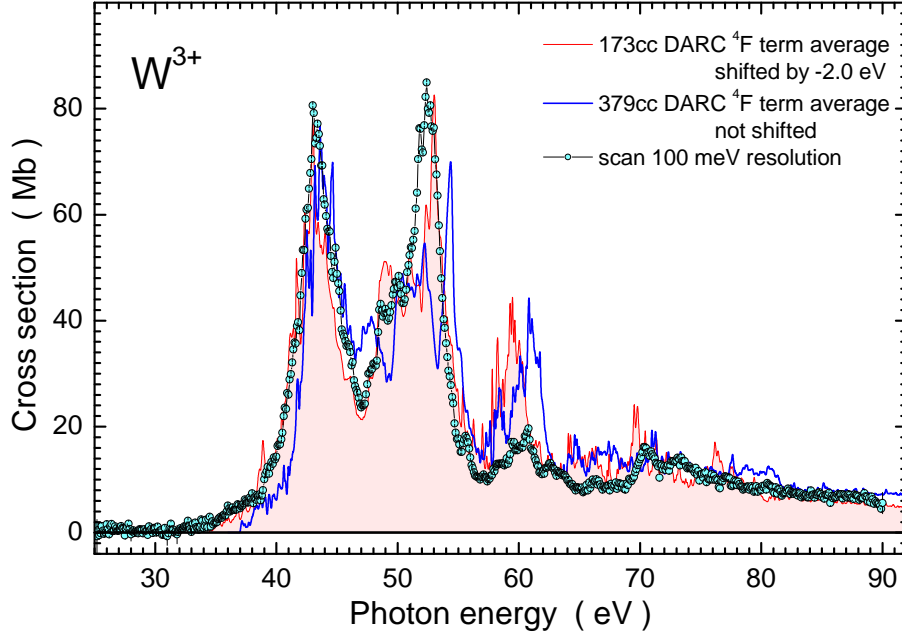


**Fig. 4** Photoionization of  $W^{2+}$  ions measured at energy resolution 100 meV. Energy-scan measurements (small circles with statistical error bars) were normalized to absolute cross-section data represented by large circles with total error bars. The black vertical bars at energies below 26 eV represent ionization thresholds of all  $5d^4$ ,  $5d^36s$ , and  $5d^26s^2$  levels with excitation energies lower than the excitation energy of the lowest level ( $^3G_2$ ) within the  $5d^36p$  configuration. These thresholds were calculated by using the Cowan code [45] as implemented by Fontes and co-workers [46] and were shifted by about 0.5 eV to match the ground level ionization threshold from the NIST tables [47]. The (brown) vertical bars between 25 and 26 eV indicate the NIST ionization potentials of the levels within the  $5d^4^5D$  ground-term. The lowest (green) vertical bar which matches the cross-section onset shows the NIST ground-term-averaged ionization potential. The solid (red) line with (light red) shading represents the result of the present 392-level DARC calculation (125  $\mu$ eV step size) of the ground-term-averaged photoionization cross section, convoluted with a Gaussian of 100 meV width. The theoretical cross sections are shifted by -1.4 eV to match experiment [43].

of scattering channels. These codes are presently running on a variety of parallel high performance computing architectures world wide [7, 8, 9]. DARC calculations on photoionization of heavy ions carried out for  $Se^+$  [5],  $Xe^+$  [6],  $Fe^+$  [38],  $Xe^{7+}$  [39],  $W^+$  [40, 41, 44],  $Se^{2+}$  [42], and  $Kr^+$  [48], ions showed suitable agreement with high resolution ALS measurements. Large-scale DARC photoionization cross section calculations on neutral sulfur compared to photolysis experiments, made in Berlin [49], and measurements performed at SOLEIL for 2p removal in  $Si^+$  ions by photons [50] both showed suitable agreement.

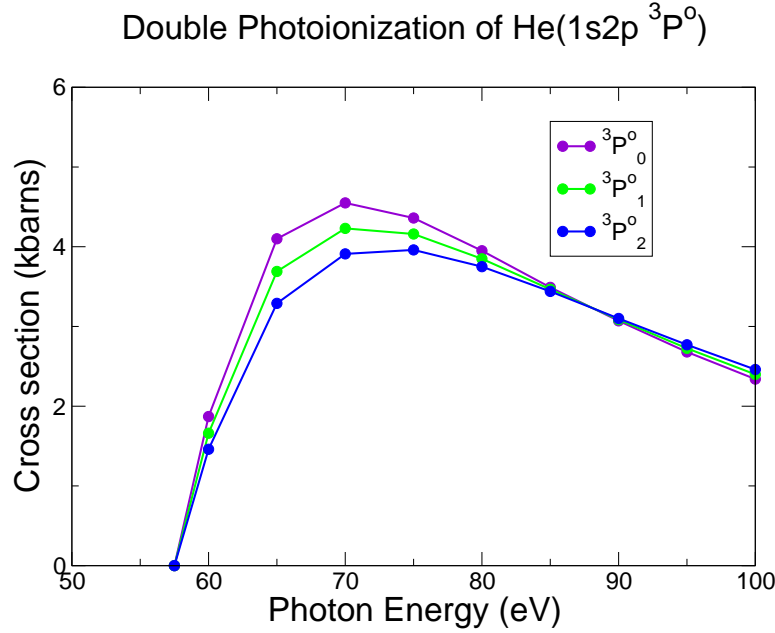
Experimental and theoretical results are reported for single-photon single ionization of  $W^{2+}$  and  $W^{3+}$  tungsten ions. Experiments were performed at the photon-ion merged-beam setup of the Advanced Light Source in Berkeley. Absolute cross sec-





**Fig. 5** Comparison of the measured photoionization cross section of  $W^{3+}$  with the present 173-level DARC calculation (87  $\mu\text{eV}$  step size; thin red line with shading) and the present 379-level DARC result (109  $\mu\text{eV}$  step size; solid blue line without shading). The theory curves were obtained by convolution of the original spectra with a Gaussian of 100 meV width. Only the 173-level calculations are shifted down in energy by 2.0 eV so that the steep rise of the experimental cross section function at about 40 eV is matched.

tions and detailed energy scans were measured over an energy range from about 20 eV to 90 eV at a bandwidth of 100 meV. Broad peak features with widths typically around 5 eV have been observed with almost no narrow resonances present in the investigated energy range. Theoretical results were obtained from a Dirac-Coulomb  $R$ -matrix approach. The calculations were carried out for the lowest-energy terms of the investigated tungsten ions with levels  $5s^25p^65d^4\ ^5D_J$ ,  $J = 0, 1, 2, 3, 4$  for  $W^{2+}$  and  $5s^25p^65d^3\ ^4F_{J'}$ ,  $J' = 3/2, 5/2, 7/2, 9/2$  for  $W^{3+}$ . As illustrated in Fig. 4 for  $W^{2+}$  ions, suitable agreement is achieved below 60 eV, but at higher energies there is a factor of approximately two difference between experiment and theory. In Fig. 5, assuming a statistically weighted distribution of ions in the initial ground-term levels, over the energy range investigated, good agreement between theory and experiment for  $W^{3+}$  ions is achieved [43].



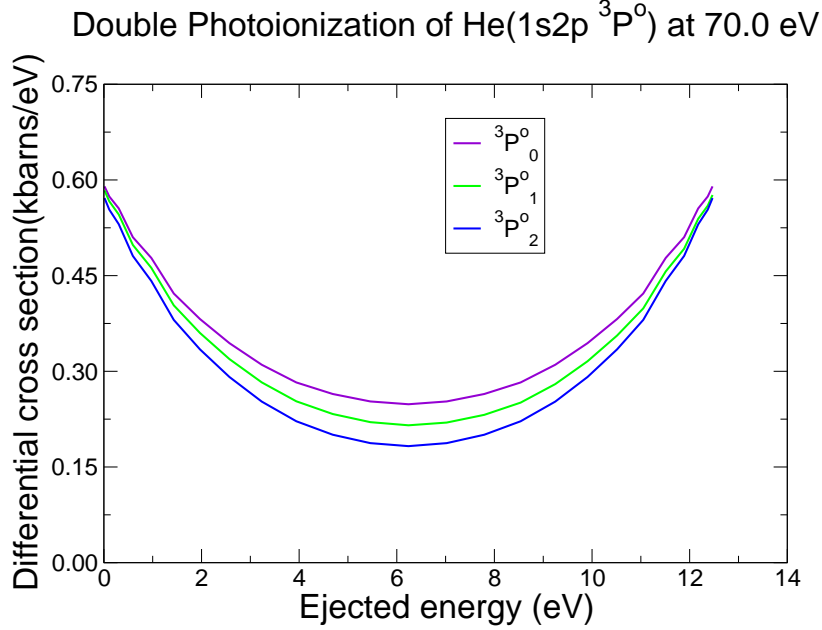
**Fig. 6** Total cross sections (kbarns) as a function of photon energy using the time dependent close-coupling (TDCC) method. Results are shown for the initial individual fine-structure states of  $\text{He}(1s2p\ ^3P^0_J)$ , where  $J=0, 1$  and  $2$  [52].

#### 4 Single-Photon Double Ionization: He

The time-dependent close-coupling (TDCC) method [51] was used to perform single-photon double ionization cross section calculations of He in the  $1s2p\ ^3P^0$  excited state. Total and energy differential cross sections for the  $1s2p\ ^3P^0$  excited state are presented for the TDCC  $(\ell_1, \ell_2, L)$  and TDCC  $(\ell_1\ j_1, \ell_2\ j_2, J)$  representations. Fig. 6 illustrates the total TDCC total cross sections, and Fig. 7 that for the differential cross section, as a function of the ejected electron energy in eV, for each initial  $\text{He}(1s2p\ ^3P^0_{0,1,2})$  fine-structure level. Differences found between the level resolved single-photon double ionization cross sections are due to varying degrees of continuum correlation found in the outgoing two electrons [52].

#### 5 Photodissociation: $\text{SH}^+$

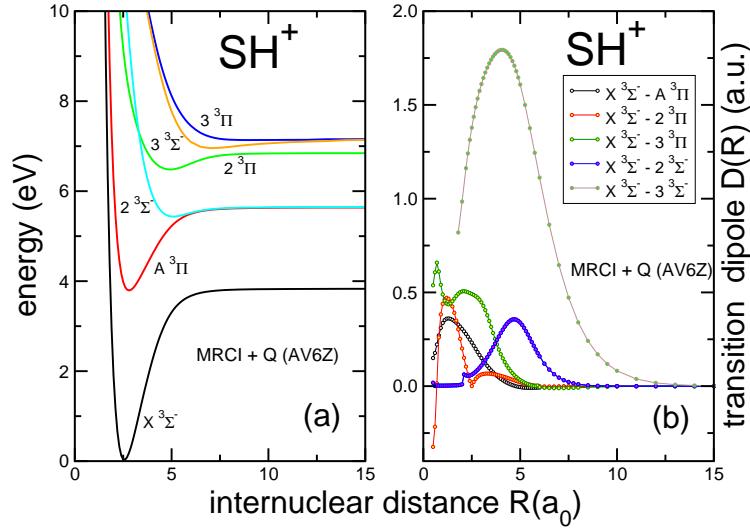
Photodissociation cross sections for the  $\text{SH}^+$  radical are computed from all rovibrational (RV) levels of the ground electronic state  $X\ ^3\Sigma^-$  for wavelengths from



**Fig. 7** Differential cross sections (kilobarns/eV) as a function of the ejected electron energy in eV using the time dependent close-coupling (TDCC) method at a photon energy of 70 eV. Results are shown for the initial individual fine-structure states of  $\text{He}(1s2p\ ^3P_J^0)$ , where  $J=0, 1$  and  $2$  [52].

threshold to 500 Å. The five electronic transitions,  $2\ ^3\Sigma^- \leftarrow X\ ^3\Sigma^-$ ,  $3\ ^3\Sigma^- \leftarrow X\ ^3\Sigma^-$ ,  $A\ ^3\Pi \leftarrow X\ ^3\Sigma^-$ ,  $2\ ^3\Pi \leftarrow X\ ^3\Sigma^-$ , and  $3\ ^3\Pi \leftarrow X\ ^3\Sigma^-$ , are treated with a fully quantum-mechanical two-state model, (i.e. no non-adiabatic coupling between excited states was included in our work). The photodissociation calculations incorporate adiabatic potential energy curves (PEC) and transition dipole moment (TDM) functions computed in the multi-reference configuration interaction approach [53] with the Davidson correction (MRCI+Q) [54], using an augmented-correlation-consistent polarized valence sextuplet basis set, designated as aug-cc-pV6Z or AV6Z, as illustrated in Fig. 8. We have adjusted our *ab initio* data to match available experimental molecular data and asymptotic atomic limits. Local thermodynamic equilibrium (LTE) photodissociation cross sections were computed which assume a Boltzmann distribution of RV levels in the  $X\ ^3\Sigma^-$  molecular state of the  $\text{SH}^+$  cation. The LTE cross sections are presented for temperatures in the range 1,000 - 10,000 K.

As far as we are aware, the current work is the first explicit photodissociation calculations for the  $\text{SH}^+$  radical ion. An estimate was made in van Dishoeck et al. [55] of the  $\text{SH}^+$  cross section by scaling that of  $\text{CH}^+$ . As illustrated in Fig. 9, there is suitable agreement, however the current results are about a factor of 3 larger,

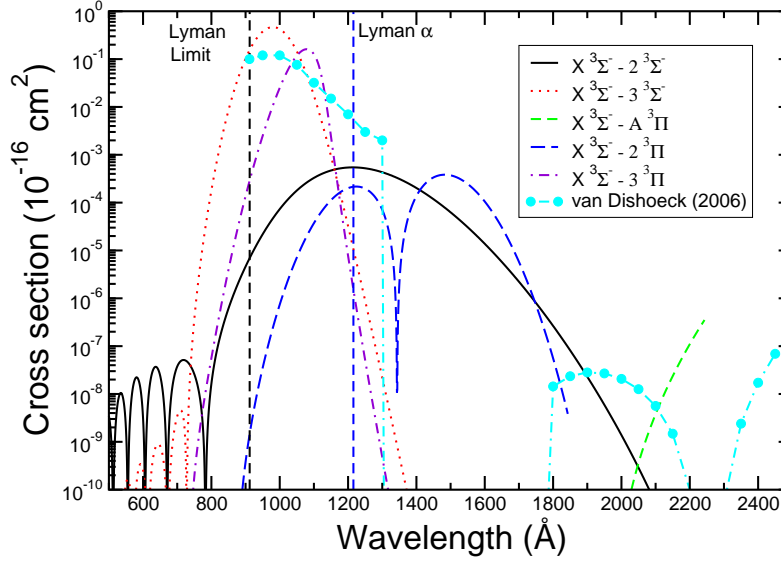


**Fig. 8** (a) Relative electronic energies (eV) for the  $\text{SH}^+$  molecular cation, as a function of bond separation at the MRCI+Q level of approximation with an AV6Z basis. Energies are relative to the ground state near equilibrium ( $2.6 a_0$ ). The states shown are for the transitions connecting the  $X^3\Sigma^- \rightarrow 2^3\Sigma^-, 3^3\Sigma^-, A^3\Pi, 2^3\Pi, 3^3\Pi$  states involved in the photodissociation process. (b) Dipole transition moments  $D(R)$  (a.u.) for the  $X^3\Sigma^- \rightarrow A^3\Pi, 2^3\Sigma^-, 3^3\Sigma^-, 2^3\Pi, 3^3\Pi$  transitions. The MRCI + Q approximation with an AV6Z basis set was used to calculate the transition dipole moments.

therefore we would expect the photodissociation rate to be enhanced by a similar amount.

In Fig.10, the LTE cross sections for all five transitions are compared at 3,000 K. This should be compared to Fig. 9 for  $v'' = 0, J'' = 0$  where it is seen that the cross sections are larger in the LTE case for wavelengths longer than  $\sim 1500 \text{ \AA}$ .

The  $\text{SH}^+$  radical ion, sulfanylium, was not detected in the interstellar medium (ISM) until as late as 2010 [56]. It is however, an important tracer of gas condensations in dense regions and also probes the warm surface layers of photo-dominated regions (PDR) [57]. Furthermore, its abundance is expected to be enhanced in x-ray dominated regions (XDR) [58]. In their model of the Orion Bar PDR, Nagy et al. [57] find that photodissociation accounts for a maximum of about 4.4% of the total destruction rate of  $\text{SH}^+$ , since reactive collisions with H and dissociative recombination by electrons are more efficient. However, they adopted the estimated cross section of [55] for  $v'' = 0, J'' = 0$ . We point out that the adoption of the current cross sections would enhance the photodissociation contribution to greater than 10%. We note that the photodissociation rates are not given here as they are sensitive to the local radiation field and dust properties. The latter is quite different in the Orion Bar

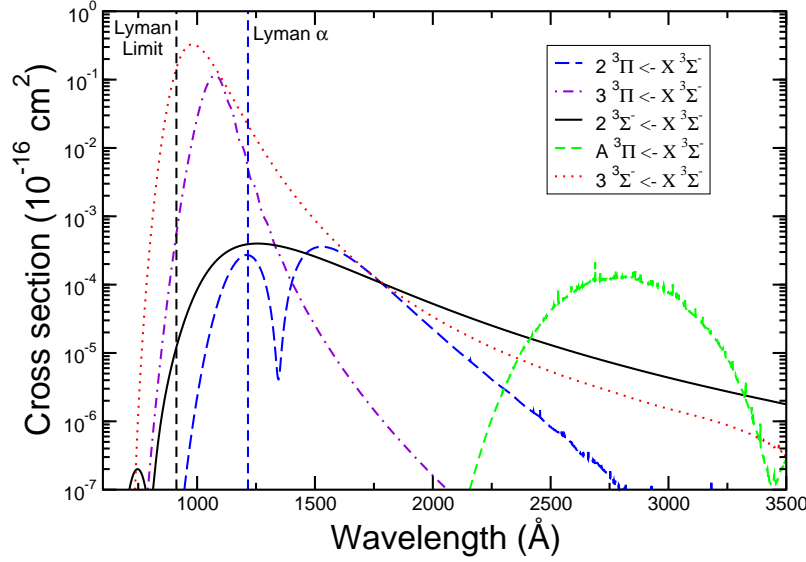


**Fig. 9** Comparison of  $\text{SH}^+$  photodissociation cross sections for  $v'' = 0$  and  $J'' = 0$  with estimates from Ref. [55].

from the average ISM of the galaxy. The densities and temperatures ( $10^5$ - $10^6 \text{ cm}^{-3}$  and  $\sim 1,000 \text{ K}$ ) of the Orion Bar PDR begin to approach the regime where photodissociation from excited states might contribute which is currently neglected in all models. Furthermore, LTE conditions are almost satisfied, but at  $1,000 \text{ K}$  there is not a significant difference between the LTE and  $v'' = 0, J'' = 0$  cross sections [59].

## 6 Summary

The power of the predictive nature of the R-matrix approach within a non-relativistic or a fully relativistic approach for photoionization cross sections, valence or inner-shell, resonance energy positions, Auger widths and strengths is illustrated. Quantal calculation of photodissociation cross sections and rates for astrophysical applications require as input accurate potential energy curves and transition dipole moments. Access to leadership architectures is essential to our research work such as the Cray-XC40 at HLRS which provides an integral contribution to our computational effort in atomic, molecular and optical collision processes.



**Fig. 10** Total  $\text{SH}^+$  LTE photodissociation cross section at 3000 K for all electronic transitions.

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